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A fresh look at ensembles: Derivative discontinuities in density functional theory

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We present a zero temperature ensemble spin density functional theory. We discuss the ensemble quantities that arise from derivative discontinuities, including the nonvanishing asymptotic potential and band gap shift, in the context of the Kohn–Sham formalism, and hybrid exact exchange theories, such as the Hartree–Fock–Kohn–Sham formalism. We describe and implement a general method of calculating these quantities in atomic and molecular systems. Finally we discuss how our results explain the deficiencies of existing functionals, and how new functionals should be constructed, illustrating our conclusions by examining the dissociation of H_2^+. © *1999 American Institute of Physics.* [S0021-9606(99)00607-8]

I. INTRODUCTION

Density functional theory[1] continues to enjoy great popularity in the chemical physics community. This is because the fundamental variable, the electron density $\rho(\mathbf{r})$, is an observable, and is also a much simpler quantity than the many body wave function or Green's function. Density functional theory is usually reformulated in the language of Hartree theory, to give the Kohn–Sham (KS) (Ref. 2) formalism, where correlation effects are described by an exchange-correlation functional $E_{\mathrm{xc}}[\rho]$, to be approximated. An alternative related approach is to describe part of the correlation using the exact exchange orbital expression, which we term the hybrid-Kohn–Sham (HyKS) formalism, popularized by Becke,[3] and formalized by Görling and Levy.[4] The Hartree–Fock–Kohn–Sham formalism (HFKS)[2,5–8] is a special case of HyKS theory, and it is also the HyKS formalism which lies behind fractional exact exchange functionals, such as B3LYP.[3] It is with the KS and HyKS theories that we are concerned in this work.

The basic theory of the density continues to be extended to new domains. Following the initial work of Mermin,[9] Perdew, Parr, Levy, and Balduz[10] reformulated the grand canonical ensemble density theory of fractional particle numbers. This has proven a useful concept, as it allows one to rigorously rewrite the variational principle as a Lagrangian minimization. In addition, the Lagrange multiplier, associated with a fixed particle number, can be associated with the chemical potential μ.

Although theoreticians have focused on modeling the properties of the zero temperature energy functional for integer numbers of particles, here we will argue that they are still implicitly working with functionals defined over the larger domain of all real particle numbers. Accordingly, it is important to understand properties of the zero temperature grand canonical (ZTGC) ensemble energy functional associated with variable particle numbers, which despite the work of previous authors[10–13] are not all well-known, and are unknown in the context of exact-exchange theories. In particular, the derivative discontinuities of the ZTGC ensemble energy functional at integer particle numbers give rise to nonvanishing asymptotic exchange-correlation and correlation potentials, and also to KS and HyKS/HFKS hardnesses/band gaps that are shifted from the true hardnesses/band gaps.

Therefore, in this work we take a fresh look at the ZTGC ensemble density functional theory. We will be concerned predominantly with atomic and molecular systems, where the ensemble theory is less used. First, in Sec. II, we recast the theory in terms of the spin density, and present the theory of the chemical potential, the asymptotic exchange-correlation and correlation potentials, and the hardness shift, in unrestricted Kohn–Sham (UKS) theory, and also investigate hybrid-Kohn–Sham (UHyKS) theory, which holds some surprises. Some additional results related to this section, including the path dependence of the energy functional derivative, and a modified Janak's theorem, are described in the Appendices. In Sec. III, we use accurate numerical potentials to calculate the actual asymptotic potentials, and the hardness shifts in atoms and molecules. In Sec. IV we describe the implications for existing and new density functionals, and demonstrate how some of the deficiencies of existing functionals in current chemical applications, can be understood. Finally in Sec. V we present our conclusions.

II. THEORY

A. Ensemble spin-density functional theory

Here we present the extension of zero temperature spin density functional theory to all real particle numbers. Although no closed physical system can have a noninteger particle number, it is possible, for example by spatial partitioning, to define open systems within such a closed system. If such open systems are sufficiently far apart so as not to overlap, then quantities such as energy and particle number become well defined in a local sense, and fractional particle numbers can arise. Such open systems are treated using grand canonical ensemble theory.

The spin density formulation is important, as it must be

used for systems in magnetic fields, and is also useful for spin-polarized systems in the absence of magnetic fields. We will be considering systems only in the absence of magnetic fields, but to eliminate spin degeneracies in the ground state, we take the magnetic field to be a positive infinitesimal, in order that any excess spin particles have α spin.

First define some notation. We use the standard α,β labels to denote spin-quantities; σ is used as a generic spin-label, and the absence of a spin-label denotes the corresponding restricted theory quantity. Also, N denotes a positive integer number of particles and M denotes any positive real number of particles. For example, N^α and N^β denote an integer number of α and β particles, respectively. Where a quantity depends on both the α and β variables, we use the compound index $\alpha\beta$. Thus $N^{\alpha\beta}$ denotes the quantity (N^α,N^β); the parentheses denote ''evaluated at.'' Finally, unless otherwise indicated, ensemble means grand canonical ensemble, in the zero temperature limit, and all derivatives are taken with the external potential held fixed.

Now consider an ensemble of spin particles, which is characterized by average particle numbers M^σ, spin chemical potentials μ^σ, and equilibrium density operator $\hat{\Gamma}$. The equilibrium (ground-ensemble) density $\rho_0^{\alpha\beta}$ minimizes the grand canonical potential Ω at fixed external potential $v_{\text{ext}}(\mathbf{r})$, where $\Omega[\rho^{\alpha\beta}]$ is defined by,

$$\Omega[\rho^{\alpha\beta}] = \min_{\hat{\Gamma}\to\rho^{\alpha\beta}} \mathrm{Tr}[(\hat{H}-\mu^\alpha M^\alpha-\mu^\beta M^\beta)\hat{\Gamma}] \tag{1}$$

$$= E[\rho^{\alpha\beta}]-\mu^\alpha M^\alpha-\mu^\beta M^\beta. \tag{2}$$

Minimization of $\Omega[\rho^{\alpha\beta}]$ with respect to the spin density ρ^σ, amounts to a Lagrangian minimization of the ensemble energy functional $E[\rho^{\alpha\beta}]$ with the constraint of $M^{\alpha\beta}$ particles. This yields the Euler–Lagrange equation,

$$\left[\frac{\delta E[\rho^{\alpha\beta}]}{\delta\rho^\sigma}-\mu^\sigma\right]_{\rho_0^{\alpha\beta}}=0. \tag{3}$$

Equation (3) is the basic working equation of ensemble spin-density functional theory. The Lagrange multiplier, may be identified as the spin chemical potential μ^σ, through the choice

$$\mu^\sigma=\partial E_0/\partial M^\sigma=(\delta E/\delta\rho^\sigma)_{\rho_0^{\alpha\beta}}, \tag{4}$$

where we have introduced the subscript 0 for ground-ensemble properties, e.g., $E_0=E[\rho_0^{\alpha\beta}]$. [It may seem odd that we use the phrase ''through the choice.'' This is because $\delta E[\rho^{\alpha\beta}]/\delta\rho^\sigma$ is not uniquely defined at $\rho_0^{\alpha\beta}$, if $E[\rho^{\alpha\beta}]$ is not smooth (a scenario which arises in this work) and thus also the Lagrange multiplier μ^σ is not uniquely defined. Instead we must make some choice, which we do through Eq. (4), properly defining μ^σ and also the energy functional derivative at $\rho_0^{\alpha\beta}$ (4). More details are provided in Appendix A.]

For atomic and molecular systems, $E_0(M^{\alpha\beta})$ is known experimentally to be a convex function of $M^{\alpha\beta}$.[6,11,14] As a consequence of convexity,[10] between integer particle numbers N and $N+1$, the ground-state density operator $\hat{\Gamma}$ linearly interpolates between the N and $N+1$ pure state density matrices. Using this, we find for the ground-state energy of a system with $N^\alpha\pm\omega^\alpha$, $N^\beta\pm\omega^\beta$ $(0<\omega^\alpha,\ \omega^\beta<1)$ electrons,

$$\begin{aligned}E_0(N^\alpha\pm\omega^\alpha,N^\beta\pm\omega^\beta)=&(1-\omega^\alpha-\omega^\beta)E_0(N^{\alpha\beta})\\&+\omega^\alpha E_0(N^\alpha\pm1,N^\beta)\\&+\omega^\beta E_0(N^\alpha,N^\beta\pm1).\end{aligned} \tag{5}$$

For integer numbers of particles, we recover the correct ground-state energy, demonstrating the equivalence of the Lagrangian minimization (3) to the pure state minimization $\min_{\Psi\to\rho_0^{\alpha\beta}}\langle\Psi|\hat{H}|\Psi\rangle$, where $\rho_0^{\alpha\beta}(\mathbf{r})$ is the ground state density. Note also that $E_0(M^{\alpha\beta})$ is given by linear interpolation as a series of straight line segments, in agreement with the analysis by Perdew *et al.*,[10] and that there are possible derivative discontinuities at $N^{\alpha\beta}$. The linear interpolation scheme for noninteger particle numbers also applies to quantities such as the density, thus

$$\rho_0(N^{\alpha\beta}\pm\omega^\sigma,\mathbf{r})=(1-\omega^\sigma)\rho_0(N^{\alpha\beta},\mathbf{r})+\omega^\sigma\rho_0(N^{\alpha\beta}\pm1^\sigma,\mathbf{r}). \tag{6}$$

Defining the ionization energy $I^\sigma(N^{\alpha\beta})$ and the electron affinity $A^\sigma(N^{\alpha\beta})$ as

$$I^\sigma(N^{\alpha\beta})=E_0(N^{\alpha\beta}-1^\sigma)-E_0(N^{\alpha\beta}), \tag{7}$$

$$A^\sigma(N^{\alpha\beta})=E_0(N^{\alpha\beta})-E_0(N^{\alpha\beta}+1^\sigma), \tag{8}$$

Eq. (5) then yields for the derivative of the energy, the spin chemical potential μ^σ,

$$\mu^\sigma(N^{\alpha\beta}+\omega^\sigma)=-A^\sigma(N^{\alpha\beta}), \tag{9}$$

$$\mu^\sigma(N^{\alpha\beta}-\omega^\sigma)=-I^\sigma(N^{\alpha\beta}), \tag{10}$$

$$\mu^\sigma(N^{\alpha\beta})=-\tfrac{1}{2}[I^\sigma(N^{\alpha\beta})+A^\sigma(N^{\alpha\beta})]. \tag{11}$$

Note that at the integer, in Eq. (11), following Perdew *et al.*,[10] we have chosen to take the limit of $\omega^\sigma\to0$ before taking the limit of zero temperature, which gives the chemical potential at $N^{\alpha\beta}$ as an average of left and right derivatives. This definition of the chemical potential has important consequences for our later discussion.

A quantity related to the chemical potential, and which is of importance in molecular systems, is the absolute hardness of Parr and Pearson.[20] (In larger molecular systems, and solids, this quantity is more easily recognized as half the band gap.[15] We will, in general, refer to this quantity as the hardness, however.) Define the σ hardness $\Delta^\sigma(N^{\alpha\beta})$ as

$$\Delta^\sigma(N^{\alpha\beta})=\tfrac{1}{2}[I^\sigma(N^{\alpha\beta})-A^\sigma(N^{\alpha\beta})]. \tag{12}$$

Using Eqs. (9) and (10), $\Delta^\sigma(N^{\alpha\beta})$ can then be rewritten in terms of the spin chemical potential off integer

$$\Delta^\sigma(N^{\alpha\beta})=\tfrac{1}{2}[\mu^\sigma(N^{\alpha\beta}+\omega^\sigma)-\mu^\sigma(N^{\alpha\beta}-\omega^\sigma)]. \tag{13}$$

B. Chemical potential quantities in UKS and UHyKS theory

The analysis of the previous section is applicable to systems defined by *any* Hamiltonian, so long as $E_0(M^{\alpha\beta})$ remains convex [and thus Eq. (5) holds]. Two particularly important systems are the reference systems of UKS and UHyKS theory. Reference systems are chosen as convenient

alternative systems, which, at some specified particle number ($M^{\alpha\beta *}$ say), are tethered to minimize with exactly the same ground state density as the true interacting system, the idea then being that the properties of the reference system at $M^{\alpha\beta *}$ will be useful representations of the corresponding properties of the interacting system. Here we use the theory of the spin chemical potential to deduce results for reference system eigenvalues, ionization energies, and electron affinities. Subscripts *s* and *r* denote UKS and UHyKS quantities, respectively, where there is ambiguity.

The UKS reference system is a noninteracting system where the α and β electrons move in separate external constraint potentials $v_s^{\alpha}(\mathbf{r})$ and $v_s^{\beta}(\mathbf{r})$. At integer particle numbers, the ground-state wave function is a Slater determinant of spin–orbitals $\phi_i^{\sigma}(\mathbf{r})$, and at noninteger particle numbers, the density operator is given by the linear interpolation of Sec. II A.

We write the energy functional for the UKS reference system with density $\rho^{\alpha\beta}(\mathbf{r})$ as

$$E_s[\rho^{\alpha\beta}]=T_s[\rho^{\alpha\beta}]+\int \rho^{\alpha}(\mathbf{r})v_s^{\alpha}(\mathbf{r})d\mathbf{r}+\int \rho^{\beta}(\mathbf{r})v_s^{\beta}(\mathbf{r})d\mathbf{r}, \tag{14}$$

where $T_s[\rho^{\alpha\beta}]$ and the density $\rho^{\sigma}(\mathbf{r})$, for general particle numbers $N^{\alpha\beta}\pm\omega^{\sigma}$, are

$$T_s(N^{\alpha\beta}\pm\omega^{\sigma})=\min_{\{\phi_i^{\sigma}\}\to\rho^{\sigma}}\left[\sum_{i\sigma'}^{N^{\sigma'}}\langle\phi_i^{\sigma'}|-\frac{1}{2}\nabla^2|\phi_i^{\sigma'}\rangle \pm\omega^{\sigma}\langle\phi^{\sigma}_{N^{\sigma}\pm 1^{\sigma}}|-\frac{1}{2}\nabla^2|\phi^{\sigma}_{N^{\sigma}\pm 1^{\sigma}}\rangle\right], \tag{15}$$

$$\rho^{\sigma}(N^{\sigma}\pm\omega^{\sigma},\mathbf{r})=\left(\sum_i^{N^{\sigma}}[\phi_i^{\sigma}(\mathbf{r})]^2\right)\pm\omega^{\sigma}[\phi^{\sigma}_{N^{\sigma}\pm 1}(\mathbf{r})]^2. \tag{16}$$

From Eq. (15), the ground state orbitals $\phi_i^{\sigma}(\mathbf{r})$ are given by minimizing $E_s[\rho^{\alpha\beta}]$ with respect to the orbitals [at fixed $v_s^{\sigma}(\mathbf{r})$, and subject to orthonormality constraints], and are the solutions of Hartree-type UKS equations (given later) with an effective potential $v_s^{\sigma}(\mathbf{r})$.

At the UKS ground-state density $\rho_s^{\alpha\beta}(\mathbf{r})$, associated with a given $v_s^{\sigma}(\mathbf{r})$, there is a Euler equation of the form (3), namely,

$$\left[\frac{\delta E_s[\rho^{\alpha\beta}]}{\delta\rho^{\sigma}}-\mu_s^{\sigma}\right]_{\rho_s^{\alpha\beta}}=0. \tag{17}$$

The constraint potential $v_s^{\sigma}(\mathbf{r})$ is then determined, by requiring, at some specified particle number $M^{\alpha\beta *}$, the UKS reference system to minimize with the same ground state density as the interacting system, $\rho_0^{\alpha\beta}(\mathbf{r})$. Partitioning the interacting ensemble energy functional

$$E[\rho^{\alpha\beta}]=T_s[\rho^{\alpha\beta}]+J_s[\rho^{\alpha\beta}]+E_{xc}[\rho^{\alpha\beta}]+\int\rho(\mathbf{r})v_{\mathrm{ext}}(\mathbf{r})d\mathbf{r} \tag{18}$$

(where the Coulomb energy $J_s[\rho^{\alpha\beta}]=\frac{1}{2}\int\int[\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)/r_{12}]d\mathbf{r}_1d\mathbf{r}_2$ and $E_{\mathrm{xc}}[\rho^{\alpha\beta}]$ is the usual exchange-correlation functional), and comparing the Euler equations (3) and (17), yields the required constraint potential $v_s^{\sigma}(\mathbf{r})$ as

$$\begin{aligned}v_s^{\sigma}(\mathbf{r})&=v_{\mathrm{ext}}(\mathbf{r})+\left[\frac{\delta J_s[\rho^{\alpha\beta}]}{\delta\rho^{\sigma}}\right]_{\rho_0^{\alpha\beta}(M^{\alpha\beta *})}+\left[\frac{\delta E_{\mathrm{xc}}[\rho^{\alpha\beta}]}{\delta\rho^{\sigma}}\right]_{\rho_0^{\alpha\beta}(M^{\alpha\beta *})}\\&=v_{\mathrm{ext}}(\mathbf{r})+v_J(\mathbf{r})+v_{\mathrm{xc}}^{\sigma}(\mathbf{r}).\end{aligned} \tag{19}$$

Note that we have defined $v_J(\mathbf{r})$ and $v_{\mathrm{xc}}^{\sigma}(\mathbf{r})$ as the functional derivatives of $J_s[\rho^{\alpha\beta}]$ and $E_{\mathrm{xc}}[\rho^{\alpha\beta}]$, at the ground state density $\rho_0^{\alpha\beta}(M^{\alpha\beta *})$, respectively.

Now, we see from Eqs. (15), (18), and (19) that since

$$\left[\frac{\delta E[\rho^{\alpha\beta}]}{\delta\rho^{\sigma}}\right]_{\rho_0^{\alpha\beta}(M^{\alpha\beta *})}=\left[\frac{\delta E_s[\rho^{\alpha\beta}]}{\delta\rho^{\sigma}}\right]_{\rho_0^{\alpha\beta}(M^{\alpha\beta *})}, \tag{20}$$

the spin-dependent chemical potentials $\mu_s^{\sigma}(M^{\alpha\beta *})$ of the UKS reference system and the interacting system are identical, by construction. Note also that the ground-state energy of the noninteracting reference system is simply the sum of occupied orbital eigenvalues (multiplied by their occupation number). The energy of the $N^{\alpha\beta}\pm\omega^{\sigma}$ reference system is given by the linear interpolation of Eq. (5), and thus μ_s^{σ} can be expressed in terms of the orbital eigenvalues. Using Eqs. (9), (10), and (11), as applied to the UKS reference system, and equating chemical potentials with the true system, we have for $M^{\alpha\beta *}=N^{\alpha\beta}-\omega^{\sigma}$,

$$\epsilon^{\sigma}_{\mathrm{HOMO}}(M^{\alpha\beta *})=-I^{\sigma}(N^{\alpha\beta}), \tag{21}$$

for $M^{\alpha\beta *}=N^{\alpha\beta}+\omega^{\sigma}$,

$$\epsilon^{\sigma}_{\mathrm{HOMO}}(M^{\alpha\beta *})=-A^{\sigma}(N^{\alpha\beta}), \tag{22}$$

and for $M^{\alpha\beta *}=N^{\alpha\beta}$,

$$\epsilon^{\sigma}_{\mathrm{HOMO}}(m^{\alpha\beta *})+\epsilon^{\sigma}_{\mathrm{LUMO}}(M^{\alpha\beta *})=-[I^{\sigma}(N^{\alpha\beta})+A^{\sigma}(N^{\alpha\beta})], \tag{23}$$

where $\epsilon^{\sigma}_{\mathrm{HOMO}}$ and $\epsilon^{\sigma}_{\mathrm{LUMO}}$ are the eigenvalues of the highest occupied orbital and lowest unoccupied orbital of spin σ, respectively. Equations (21) and (22) agree with the results from Janak's theorem,[16] which states that $\epsilon_i^{\sigma}=\partial E/\partial n_i^{\sigma}$, where n_i^{σ} is the occupation number of spin–orbital *i*, and which holds where $E[\rho^{\alpha\beta}]$ is differentiable. Note also that Eq. (23) defines the spin exchange-correlation potential as an average of left and right derivatives

$$v_{\mathrm{xc}}^{\sigma}(N^{\alpha\beta},\mathbf{r})=\tfrac{1}{2}[v_{\mathrm{xc}}^{\sigma}(N^{\alpha\beta},\mathbf{r})_-+v_{\mathrm{xc}}^{\sigma}(N^{\alpha\beta},\mathbf{r})_+]. \tag{24}$$

These results form the basis of our later analysis of the exchange-correlation potential $v_{\mathrm{xc}}^{\sigma}(\mathbf{r})$.

We now examine the UHyKS reference system, which is a Hartree–Fock-type interacting system, where the σ electrons move in an external constraint potential, $v_r^{\sigma}(\mathbf{r})$. As in the UKS reference system, at integer particle numbers, the ground state is represented by a Slater determinant of spin

orbitals $\phi_i^\sigma(\mathbf{r})$; while at noninteger particle numbers, the ground ensemble density operator is given by the linear interpolation of Sec. II A.

We write the UHyKS ensemble energy functional as,

$$E_r[\rho^{\alpha\beta}] = T_r[\rho^{\alpha\beta}] + \int \rho^\alpha(\mathbf{r}) v_r^\alpha(\mathbf{r}) d\mathbf{r} + \int \rho^\beta(\mathbf{r}) v_r^\beta(\mathbf{r}) d\mathbf{r} + J_r[\rho^{\alpha\beta}] + \zeta K_r[\rho^{\alpha\beta}]. \tag{25}$$

For integer particle numbers $N^{\alpha\beta}$, we have

$$T_r(N^{\alpha\beta}) = \sum_{i\sigma}^{N^\sigma} \langle \phi_i^\sigma(N^{\alpha\beta},\mathbf{r}) | -\frac{1}{2}\nabla^2 | \phi_i^\sigma(N^{\alpha\beta},\mathbf{r}) \rangle, \tag{26}$$

$$J_r(N^{\alpha\beta}) = \frac{1}{2}\int\int \sum_{ij\sigma\sigma'}^{N^\sigma N^{\sigma'}} [\phi_i^\sigma(N^{\alpha\beta},\mathbf{r}_1)]^2 \times \frac{1}{r_{12}} [\phi_j^{\sigma'}(N^{\alpha\beta},\mathbf{r}_2)]^2 d\mathbf{r}_1 d\mathbf{r}_2, \tag{27}$$

$$K_r(N^{\alpha\beta}) = -\frac{1}{2}\int\int \sum_{ij\sigma}^{N^\sigma} \phi_i^\sigma(N^{\alpha\beta},\mathbf{r}_1)\phi_i^\sigma(N^{\alpha\beta},\mathbf{r}_2) \times \frac{1}{r_{12}} \phi_j^\sigma(N^{\alpha\beta},\mathbf{r}_1)\phi_j^\sigma(N^{\alpha\beta},\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \tag{28}$$

$$\rho^\sigma(N^\sigma,\mathbf{r}) = \sum_i^{N^\sigma} [\phi_i^\sigma(N^{\alpha\beta},\mathbf{r})]^2, \tag{29}$$

with the orbitals defined through the constrained minimization,

$$[T_r + K_r + J_r] = \min_{\{\phi_i^\sigma \to \rho^{\alpha\beta}\}} \langle T_r + J_r + K_r \rangle. \tag{30}$$

The ground-state orbitals are solutions of Hartree–Fock-type UHyKS equations (given later) with a scaled exchange contribution, and with an effective potential $v_r^\sigma(\mathbf{r})$.

For noninteger particle numbers, ensemble quantities are defined using the linear interpolation scheme of the previous section, giving for general particle numbers $N^{\alpha\beta} \pm \omega^\sigma$,

$$T_r(N^{\alpha\beta} \pm \omega^\sigma) = (1-\omega^\sigma) T_r(N^{\alpha\beta}) + \omega^\sigma T_r(N^{\alpha\beta} \pm 1^\sigma), \tag{31}$$

$$J_r(N^{\alpha\beta} \pm \omega^\sigma) = (1-\omega^\sigma) J_r(N^{\alpha\beta}) + \omega^\sigma J_r(N^{\alpha\beta} \pm 1^\sigma), \tag{32}$$

$$K_r(N^{\alpha\beta} \pm \omega^\sigma) = (1-\omega^\sigma) K_r(N^{\alpha\beta}) + \omega^\sigma K_r(N^{\alpha\beta} \pm 1^\sigma), \tag{33}$$

$$\rho^\sigma(N^\sigma \pm \omega^\sigma,\mathbf{r}) = (1-\omega^\sigma)\rho^\sigma(N^{\alpha\beta},\mathbf{r}) + \omega^\sigma \rho^\sigma(N^{\alpha\beta} \pm 1^\sigma,\mathbf{r}). \tag{34}$$

In all the above, ζ is just a scale factor for the exact exchange K_r. ζ was originally chosen as 1;[2] this corresponds to the unrestricted-Hartree–Fock–Kohn–Sham (UHFKS) theory, though although other choices of ζ have become popular,[3] in hybrid functionals such as B3LYP. Various formal aspects of HyKS theory are considered in Görling and Levy,[4] and the implications for finite temperature theories are discussed in Chan.[8]

At the ground-state density $\rho_r^{\alpha\beta}(\mathbf{r})$ of the UHyKS reference system, associated with the constraint potential $v_r^\sigma(\mathbf{r})$, $E_r[\rho^{\alpha\beta}]$ satisfies a Euler equation

$$\left[\frac{\delta E_r[\rho^{\alpha\beta}]}{\delta\rho^\sigma} - \mu_r^\sigma\right]_{\rho_r^{\alpha\beta}} = 0. \tag{35}$$

Requiring the UHyKS reference system and interacting system to minimize at the same density $\rho_0^{\alpha\beta}(\mathbf{r})$, for particle number $M^{\alpha\beta *}$, we identify $v_r^\sigma(\mathbf{r})$ through partitioning the energy functional

$$E[\rho^{\alpha\beta}] = T_r[\rho^{\alpha\beta}] + J_r[\rho^{\alpha\beta}] + \zeta K_r[\rho^{\alpha\beta}] + E_c[\rho^{\alpha\beta}] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}, \tag{36}$$

(where using Eqs. (30) and (36), we have collectively defined a correlation energy $E_c[\rho^{\alpha\beta}]$, different for different ζ, over the range of all particle numbers) giving

$$v_r^\sigma(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \left[\frac{\delta E_c[\rho^{\alpha\beta}]}{\delta\rho^\sigma}\right]_{\rho_0^{\alpha\beta}(M^{\alpha\beta *})} = v_{\text{ext}}(\mathbf{r}) + v_c^\sigma(\mathbf{r}). \tag{37}$$

Again, since from Eqs. (30), (36), and (37),

$$\left[\frac{\delta E[\rho^{\alpha\beta}]}{\delta\rho^\sigma}\right]_{\rho_0^{\alpha\beta}(M^{\alpha\beta *})} = \left[\frac{\delta E_r[\rho^{\alpha\beta}]}{\delta\rho^\sigma}\right]_{\rho_0^{\alpha\beta}(M^{\alpha\beta *})}, \tag{38}$$

the spin chemical potentials of the UHyKS reference system and the interacting system are the same at $M^{\alpha\beta *}$, by construction. Thus using Eqs. (9), (10), (11) as applied to the UHyKS reference system, and equating chemical potentials with the interacting system, we have, for $M^{\alpha\beta *} = N^{\alpha\beta} - \omega^\sigma$,

$$I_r^\sigma(M^{\alpha\beta *}) = I^\sigma(N^{\alpha\beta}), \tag{39}$$

for $M^{\alpha\beta *} = N^{\alpha\beta} - \omega^\sigma$,

$$A_r^\sigma(M^{\alpha\beta *}) = A^\sigma(N^{\alpha\beta}), \tag{40}$$

and for $M^{\alpha\beta *} = N^{\alpha\beta}$,

$$I_r^\sigma(M^{\alpha\beta *}) + A_r^\sigma(M^{\alpha\beta *}) = I^\sigma(N^{\alpha\beta}) + A^\sigma(N^{\alpha\beta}), \tag{41}$$

where I_r^σ and A_r^σ are the σ ionization energy and electron affinity of the UHyKS reference system, respectively, that is

$$I_r^\sigma(N^{\alpha\beta}) = E_{r0}(N^{\alpha\beta} - 1^\sigma) - E_{r0}(N^{\alpha\beta}), \tag{42}$$

$$A_r^\sigma(N^{\alpha\beta}) = E_{r0}(N^{\alpha\beta}) - E_{r0}(N^{\alpha\beta} + 1^\sigma). \tag{43}$$

Recall that because the reference system is interacting, the ground state energy E_{r0} is not given by a sum of orbital energies. Instead, the ionization energy $I_r^\sigma(N^{\alpha\beta})$ is the difference between the energy of the $N^{\alpha\beta}$ Slater determinant and the relaxed $N^{\alpha\beta} - 1$ Slater determinant, in the same external potential $v_r^\sigma(\mathbf{r})$. Note also, that in the last case (41), we have defined the spin correlation potential as an average of left and right derivatives.

We see that since the UHyKS reference system is a Hartree–Fock-type system, Koopman's theorem[17] will hold, and the UKS results (21), (22), and (23) are correct in the UHyKS theory only up to (small) relaxation terms. As a

corollary, Janak's theorem, at least given by the simple form $\epsilon_i^\sigma(N^{\alpha\beta})=[\partial E_0/\partial n_i^\sigma](N^{\alpha\beta})$, where n_i^σ is the occupation number of spin–orbital $\phi_i^\sigma(N^{\alpha\beta},\mathbf{r})$, does not hold precisely in UHyKS systems. The proper extension of Janak's analysis to systems with exact exchange functionals entails some complications. For additional details the reader is referred to Appendix B.

C. The hardness shift

Although the reference system chemical potentials are identical to the interacting system chemical potentials at the point $M^{\alpha\beta *}$ where the reference system and interacting system energies minimize at the same ground state density, if $M^{\alpha\beta}=N^{\alpha\beta}$ (where the hardness is nonvanishing), Perdew and Levy,[12] and Sham and Schlüter,[13] demonstrated that the hardnesses of the reference systems and true systems differ by a quantity we term the hardness shift, with important implications for the computation of the hardness. Here we present a treatment of this quantity in the UKS and UHyKS theory.

Using the definition of the chemical potential (3), the expression for the hardness in terms of the chemical potential (13), and the UKS partitioning of the ensemble energy functional, (18) we can rewrite the hardness $\Delta^\sigma(N^{\alpha\beta})$ as

$$\Delta^\sigma(N^{\alpha\beta})=\frac{1}{2}\left[\left(\frac{\delta T_s}{\delta\rho^\sigma}\right)_+-\left(\frac{\delta T_s}{\delta\rho^\sigma}\right)_-\right]_{\rho_0^{\alpha\beta}(N^{\alpha\beta})}+\frac{1}{2}\left[\left(\frac{\delta E_{\mathrm{xc}}}{\delta\rho^\sigma}\right)_+-\left(\frac{\delta E_{\mathrm{xc}}}{\delta\rho^\sigma}\right)_-\right]_{\rho_0^{\alpha\beta}(N^{\alpha\beta})}. \tag{44}$$

Applying (13) to the UKS reference system, the first term is identified as the UKS reference system hardness, and so we can express (44) as

$$\Delta^\sigma(N^{\alpha\beta})=\tfrac{1}{2}[\epsilon^\sigma_{\mathrm{LUMO}}(N^{\alpha\beta})-\epsilon^\sigma_{\mathrm{HOMO}}(N^{\alpha\beta})]+\Delta^\sigma_{\mathrm{xc}}(N^{\alpha\beta}), \tag{45}$$

where we have introduced $\Delta^\sigma_{\mathrm{xc}}(N^{\alpha\beta})$ as the UKS hardness shift. This is the exchange-correlation contribution to the hardness, and it arises from the derivative discontinuity of the exchange-correlation functional at $N^{\alpha\beta}$. We do not expect the UKS hardness to be very similar to that of the interacting system, and thus $\Delta^\sigma_{\mathrm{xc}}(N^{\alpha\beta})$ may be expected to be relatively large. The hardness therefore requires a separate calculation of I^σ and A^σ, and cannot be obtained from a single Kohn–Sham calculation. Of course, this also implies that bandgaps calculated with the approximation $[\epsilon^\sigma_{\mathrm{LUMO}}(N^{\alpha\beta})-\epsilon^\sigma_{\mathrm{HOMO}}(N^{\alpha\beta})]$, are unlikely to be accurate, as there is no Koopmans' theorem for the UKS HOMO and LUMO eigenvalues. Sham and Schlüter[13] have provided a formal expression for Δ_{xc} from the many-body theory.

In the UHyKS theory, we follow the above analysis to obtain

$$\Delta^\sigma(N^{\alpha\beta})=\tfrac{1}{2}[I_r^\sigma(N^{\alpha\beta})-A_r^\sigma(N^{\alpha\beta})]+\Delta_c^\sigma(N^{\alpha\beta}). \tag{46}$$

$\Delta_c^\sigma(N^{\alpha\beta})$ is the UHyKS hardness shift, which is the correlation contribution to the hardness, and also arises from the derivative discontinuity of the correlation functional at $N^{\alpha\beta}$. When ζ is 1, the corresponding UHFKS reference system is fairly similar to the interacting system, and we expect $\Delta_c^\sigma(N^{\alpha\beta})$ to be reasonably small. In Sec. III B, we present calculations of the UHFKS $\Delta^\sigma_{\mathrm{xc}}(N^{\alpha\beta})$ and $\Delta_c^\sigma(N^{\alpha\beta})$.

D. The shifted exchange-correlation and correlation potentials

A quantity which is of evident interest, and which has generated some controversy, is the asymptotic limit of the ensemble spin exchange-correlation potential $v^\sigma_{\mathrm{xc}}(\mathbf{r})$ and the ensemble spin correlation potential $v_c^\sigma(\mathbf{r})$. Our work in this section extends the original analysis by Perdew *et al.*,[10–12] for $v_{\mathrm{xc}}(\mathbf{r})$, and Krieger, Li, and Iafrate, for the spin OEP,[18] to these quantities. We will find it useful to introduce exchange-correlation potentials and correlation potentials that are parallel to the ensemble potentials, but which vanish at infinity. These auxilliary quantities we denote $\overline{v}^\sigma_{\mathrm{xc}}(\mathbf{r})$ and $\overline{v}_c^\sigma(\mathbf{r})$; we also use barred symbols for eigenvalues and other quantities calculated with these potentials.

We begin by deriving some results for the exchange-correlation potential for $N^{\alpha\beta}$ particles, and thereby achieve a link with the hardness shifts of the previous sections. The exchange-correlation potential, is defined up to a constant, that is

$$v^\sigma_{\mathrm{xc}}(\mathbf{r})=\overline{v}^\sigma_{\mathrm{xc}}(\mathbf{r})+C^\sigma_{\mathrm{xc}}, \tag{47}$$

where C^σ_{xc} is the shift in the σ potential from an asymptotically vanishing potential, and is therefore the asymptotic limit of the ensemble potential $v^\sigma_{\mathrm{xc}}(\mathbf{r})$. This constant is independent from the trivial additive constant associated with the Hohenberg–Kohn theorem, and by taking appropriate limits under appropriate conditions (as below) we can give it a precise value. From the orbital equations

$$[-\tfrac{1}{2}\nabla_1^2+v^\sigma_{\mathrm{ext}}(\mathbf{r}_1)+v_J(\mathbf{r}_1)+v^\sigma_{\mathrm{xc}}(\mathbf{r}_1)]\phi_i^\sigma(\mathbf{r}_1)=\epsilon_i^\sigma\phi_i^\sigma(\mathbf{r}_1), \tag{48}$$

$$[-\tfrac{1}{2}\nabla_1^2+v^\sigma_{\mathrm{ext}}(\mathbf{r}_1)+v_J(\mathbf{r}_1)+\overline{v}^\sigma_{\mathrm{sc}}(\mathbf{r}_1)]\phi_i^\sigma(\mathbf{r}_1)=\overline{\epsilon}_i^\sigma\phi_i^\sigma(\mathbf{r}_1), \tag{49}$$

where $v_J(\mathbf{r}_1)=\int\rho(\mathbf{r}_2)/r_{12}d\mathbf{r}_2$, it is clear from equating chemical potentials in Eq. (11) that

$$\overline{\epsilon}^\sigma_{\mathrm{LUMO}}+\overline{\epsilon}^\sigma_{\mathrm{HOMO}}+2C^\sigma_{\mathrm{xc}}=-(I^\sigma+A^\sigma). \tag{50}$$

This is an important result for our later calculations.

We can further put bounds on the asymptotic limit C^σ_{xc}. Using the long range behavior of the density,[19] we have the equality

$$\epsilon^\sigma_{\mathrm{HOMO}}-v^\sigma_{\mathrm{xc}}(\infty)=-I^\sigma, \tag{51}$$

and we deduce that

$$C^\sigma_{\mathrm{xc}}\leqslant\frac{(I^\sigma-A^\sigma)}{2}. \tag{52}$$

Recall that $(I^\sigma-A^\sigma)/2$ is the spin counterpart of the absolute hardness.[20]

Next we link the asymptotic ensemble potential to the hardness shift of Sec. II C. Noting that we can substitute

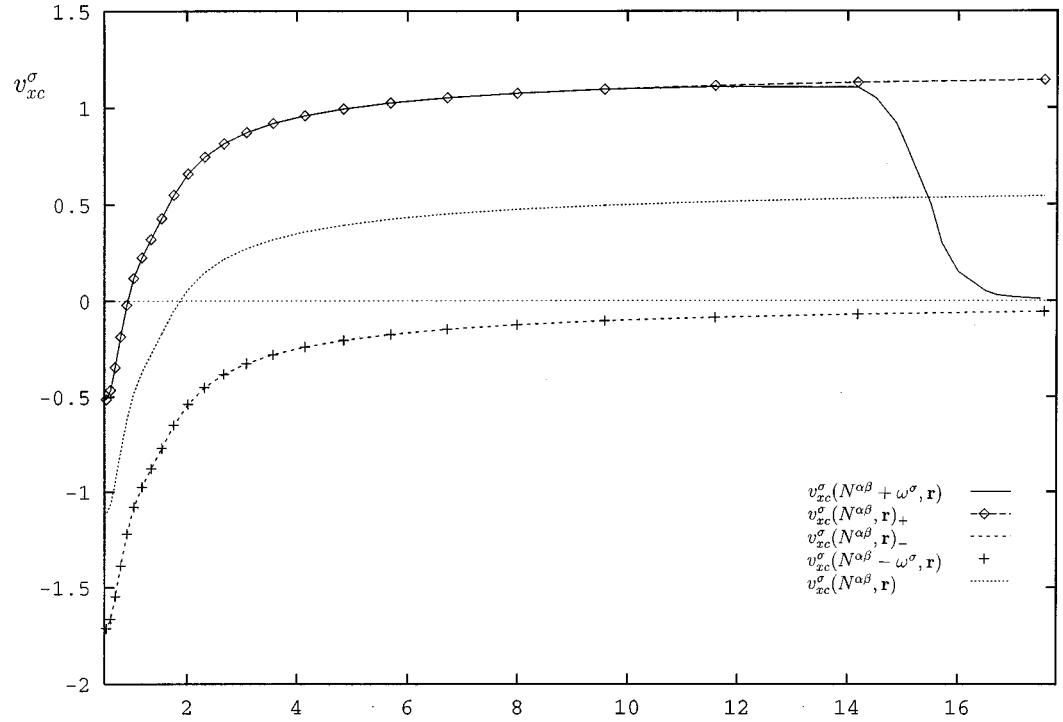

FIG. 1. A schematic diagram of the functional derivatives of $E_{\mathrm{xc}}[\rho^{\alpha\beta}]$. Shown are the left and right derivatives, $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})$, the integer exchange-correlation potential $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta})$, and the exchange-correlation potential for systems with $N^{\alpha\beta}+\omega^{\sigma}$ and $N^{\alpha\beta}-\omega^{\sigma}$ particles, $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta}+\omega^{\sigma},\mathbf{r})$ and $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta}-\omega^{\sigma},\mathbf{r})$, respectively, where ω^{σ} is a very small positive number. See Sec. II D for more details.

$\overline{\epsilon}^{\sigma}_{\mathrm{LUMO}}$ and $\overline{\epsilon}^{\sigma}_{\mathrm{HOMO}}$ in the expression for the hardness (45), and then comparing with Eq. (50) and using $\overline{\epsilon}^{\sigma}_{\mathrm{HOMO}}=-I^{\sigma}$, we have simply

$$C^{\sigma}_{\mathrm{xc}}=\Delta^{\sigma}_{\mathrm{xc}}. \tag{53}$$

Additionally, since $\Delta^{\sigma}_{\mathrm{xc}}$ is the difference of left and right derivatives, and $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})$ is the average, we can through Eqs. (24), (47), and (53), eliminate to find for $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})_{-}$ and $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})_{+}$, giving

$$v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})_{-}=\overline{v}^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r}), \tag{54}$$

$$v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})_{+}=\overline{v}^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})+2\Delta^{\sigma}_{\mathrm{xc}}. \tag{55}$$

The left-hand derivative asymptotically vanishes; the right-hand derivative is shifted up by an amount equivalent to the hardness shift.

We now consider the exchange-correlation potential for noninteger numbers of particles. Recall that the ground-state density of the $N^{\alpha\beta}\pm\omega^{\sigma}$ ensemble is

$$\rho^{\sigma}_{0}(N^{\alpha\beta}\pm\omega^{\sigma},\mathbf{r})=(1-\omega^{\sigma})\rho^{\sigma}_{0}(N^{\alpha\beta},\mathbf{r})+\omega^{\sigma}\rho^{\sigma}_{0}(N^{\alpha\beta}\pm 1^{\sigma},\mathbf{r}). \tag{56}$$

From the long range behavior of the density (51), and the behavior of the highest occupied orbital eigenvalue (9), (10), we immediately obtain

$$v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta}\pm\omega^{\sigma},\infty)=0. \tag{57}$$

In addition, the behavior of the ensemble potential will depend on the system which dominates the ensemble density, (56). Thus we have the following limits:

$$\lim_{\omega^{\sigma}\to 0}\lim_{r\to\infty} v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta}\pm\omega^{\sigma},\mathbf{r})=0, \tag{58}$$

$$\lim_{r\to\infty}\lim_{\omega^{\sigma}\to 0} v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta}+\omega^{\sigma},\mathbf{r})=2\Delta^{\sigma}_{\mathrm{xc}}. \tag{59}$$

We reconcile Eq. (58) with Eq. (59) by understanding that when we take the limit of $\omega^{\sigma}\to 0$ from above, then the region where the decay of the ensemble density is dominated by the $N^{\alpha\beta}+1^{\sigma}$ density, and where the potential vanishes asymptotically, is pushed back to infinity; it is replaced by a region where the ensemble density is dominated by the $N^{\alpha\beta}$ density, with a potential like $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})_{+}$, which goes asymptotically to $\Delta^{\sigma}_{\mathrm{xc}}$. The exchange-correlation potential then develops a jump at infinity, and the order of limits in Eqs. (58) and (59) becomes important.[12] The behavior of the various derivatives is summarized in Fig. 1.

The above analysis is equally applicable to the UHyKS correlation potential. For example, denoting the shift of the correlation potential (at $N^{\alpha\beta}$) from the asymptotically vanishing potential $\overline{v}^{\sigma}_{c}(\mathbf{r})$, C^{σ}_{c}, equating chemical potentials, and using the energy expression (25), yields the UHyKS analog of Eq. (50),

$$\overline{I}^{\sigma}_{r}+\overline{A}^{\sigma}_{r}-2C^{\sigma}_{c}=I^{\sigma}+A^{\sigma}, \tag{60}$$

a result which we use later in our calculations. Note that since the reference system ionization energies and electron affinities are expected to be reasonable approximations to the true ionization energies and electron affinities, C^{σ}_{c} should be small.

However, in applying the rest of the UKS analysis to the UHyKS theory for the corresponding correlation potential

quantities, we must not forget that using Koopmans' theorem, and equating the the long range behavior of the UHyKS density,[21] $\exp[-2(-2\overline{\epsilon}^{\sigma}_{\mathrm{HOMO}})^{1/2}r]$, with that of $\rho_0^{\alpha\beta}(\mathbf{r})$, we have

$$\overline{I}^{\sigma}_r(N^{\alpha\beta}) = -\overline{\epsilon}^{\sigma}_{\mathrm{HOMO}}(N^{\alpha\beta}) + R^{\sigma}(N^{\alpha\beta}) \tag{61}$$

$$= I^{\sigma}(N^{\alpha\beta}) + R^{\sigma}(N^{\alpha\beta}). \tag{62}$$

where we have defined the usual relaxation correction $R^{\sigma}(N^{\alpha\beta})$ of Koopmans' theorem. This means the equations obtained from the UKS analysis will have additional terms of $R^{\sigma}(N^{\alpha\beta})$. Using this, it is straightforward to arrive at the main results summarized below,

$$\Delta_c^{\sigma} = C_c^{\sigma} - R^{\sigma}(N^{\alpha\beta}), \tag{63}$$

$$v_c^{\sigma}(N^{\alpha\beta},\mathbf{r})_{\pm} = \overline{v}_c^{\sigma}(N^{\alpha\beta},\mathbf{r}) + C_c^{\sigma} \pm \Delta_c^{\sigma}, \tag{64}$$

$$\lim_{r\to\infty} v_c(N^{\alpha\beta} - \omega^{\sigma},\mathbf{r}) = R^{\sigma}(N^{\alpha\beta}), \tag{65}$$

$$\lim_{r\to\infty} v_c(N^{\alpha\beta} + \omega^{\sigma},\mathbf{r}) = R^{\sigma}(N^{\alpha\beta} + 1^{\sigma}), \tag{66}$$

$$\lim_{r\to\infty}\lim_{\omega^{\sigma}\to 0} v_c(N^{\alpha\beta} + \omega^{\sigma},\mathbf{r}) = C_c^{\sigma} + \Delta_c^{\sigma}. \tag{67}$$

Note that the correlation potential *does not* (*except by chance*) *vanish asymptotically in any system*, but instead goes asymptotically to some small constant, a limit which has been neglected in the past. Calculations of these quantities using the UHFKS ($\zeta = 1$) theory are presented in the next section.

III. CALCULATIONS

It is interesting and important to compute the various ensemble quantities described in the theory section above. Here we calculate the hardness shifts $\Delta_{\mathrm{xc}}^{\sigma}$ and Δ_c^{σ} of Sec. II C, and also the asymptotic limits of the exchange-correlation and correlation potentials described in Sec. II D, C_{xc}^{σ} and C_c^{σ}, which are of use in the construction of new functionals. For the calculation of these quantities, in addition to data for I^{σ} and A^{σ}, we require accurate numerical spin exchange-correlation and correlation potentials. These we generate from *ab initio* densities using the Zhao–Morrison–Parr[22] procedure.

A. The calculation of numerical potentials

Following the constrained search of Levy and Perdew,[23] Zhao, Morrison, and Parr[22] described a practical scheme for the computation of asymptotically vanishing exchange-correlation potentials from accurate input densities (for $N^{\alpha\beta}$ particles). We have implemented this scheme to compute asymptotically vanishing spin exchange-correlation potentials $\overline{v}^{\sigma}_{\mathrm{xc}}(\mathbf{r})$ and correlation potentials $\overline{v}^{\sigma}_c(\mathbf{r})$. Although we have worked throughout with the UHFKS formalism, which corresponds to a choice of $\zeta = 1$ in Eq. (25), the method is equally applicable to any other choice of ζ. A detailed discussion of our implementation of the Zhao–Morrison–Parr method, and the accuracy of the exchange-correlation and correlation potentials thereby calculated may be found in Ingamells and Handy,[24] Tozer, Ingamells, and Handy,[25] and Chan, Tozer, and Handy.[26]

We can define the orbital dependent functionals $T_s[\phi_i^{\sigma}]$, $T_r[\phi_i^{\sigma}]$, $J_r[\phi_i^{\sigma}]$, and $K_r[\phi_i^{\sigma}]$, through a constrained minimization, where the Kohn–Sham and Hartree–Fock–Kohn–Sham determinants are constrained to give the exact density $\rho_0^{\alpha\beta}(\mathbf{r})$, which in our case shall be some input *ab initio* density. Following Zhao, Morrison, and Parr, we enforce the constrained minimization through a Lagrange multiplier λ associated with the self-repulsion quantity I,

$$I = \frac{1}{2}\sum_{\sigma}\int\int \frac{[\rho^{\lambda\sigma}(\mathbf{r}_1) - \rho_0^{\sigma}(\mathbf{r}_1)][\rho^{\lambda\sigma}(\mathbf{r}_2) - \rho_0^{\sigma}(\mathbf{r}_2)]}{r_{12}} \times d\mathbf{r}_1 d\mathbf{r}_2, \tag{68}$$

where

$$\rho^{\lambda\sigma}(\mathbf{r}) = \sum_i \phi_i^{\lambda\sigma}(\mathbf{r})^2. \tag{69}$$

To ensure the final equations are recognizable, before minimizing with respect to the orbitals, we add explicit functionals of the density (which will not affect the minimizing orbitals)

$$\text{UKS:}\quad \int \rho^{\lambda\sigma}(\mathbf{r}_1) v_{\mathrm{ext}}(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2}\left(1 - \frac{1}{N^{\sigma}}\right)\sum_{\sigma\sigma'}\int\int \frac{\rho^{\lambda\sigma}(\mathbf{r}_1)\rho^{\lambda\sigma'}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \tag{70}$$

$$\text{UHFKS:}\quad \int \rho^{\lambda\sigma}(\mathbf{r}_1) v_{\mathrm{ext}}(\mathbf{r}_1) d\mathbf{r}_1. \tag{71}$$

Introducing the additional Lagrange multipliers $\overline{\epsilon}_i^{\sigma}$ for diagonal orthonormality constraints, minimization with respect to the orbitals gives the orbital equations

$$[-\tfrac{1}{2}\nabla_1^2 + v_{\mathrm{ext}}(\mathbf{r}_1) + v_J^{\lambda}(\mathbf{r}_1) + \overline{v}_{\mathrm{xc}}^{\lambda\sigma}(\mathbf{r}_1)]\phi_i^{\lambda\sigma}(\mathbf{r}_1) = \overline{\epsilon}_i^{\lambda\sigma}(\mathbf{r}_1)\phi_i^{\lambda\sigma}(\mathbf{r}_1), \tag{72}$$

$$[-\tfrac{1}{2}\nabla_1^2 + v_{\mathrm{ext}}(\mathbf{r}_1) + v_J^{\lambda}(\mathbf{r}_1) + v_K^{\lambda}(\mathbf{r}_1) + \overline{v}_c^{\lambda\sigma}(\mathbf{r}_1)]\phi_i^{\lambda\sigma}(\mathbf{r}_1) = \overline{\epsilon}_i^{\lambda\sigma}(\mathbf{r}_1)\phi_i^{\lambda\sigma}(\mathbf{r}_1), \tag{73}$$

where $v_J^{\lambda}(\mathbf{r}_1)$ is the Coulomb potential of the density $\rho^{\lambda}(\mathbf{r}_1)$, $v_K^{\lambda}(\mathbf{r}_1)$ is the Hartree–Fock exhange operator $-\int d\mathbf{r}_2 \Sigma_j[\phi_j^{\lambda\sigma}(\mathbf{r}_1)\phi_j^{\lambda\sigma}(\mathbf{r}_2)/r_{12}]P_{12}$, and the numerical exchange-correlation and correlation potentials are

$$\overline{v}_{\mathrm{xc}}^{\lambda\sigma}(\mathbf{r}_1) = -\frac{1}{N^{\sigma}}\int \frac{\rho^{\lambda\sigma}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + \lambda\int \frac{\rho^{\lambda\sigma}(\mathbf{r}_2) - \rho_0^{\sigma}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2, \tag{74}$$

$$\overline{v}_c^{\lambda\sigma}(\mathbf{r}_1) = \lambda\int \frac{\rho^{\lambda\sigma}(\mathbf{r}_2) - \rho_0^{\sigma}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2. \tag{75}$$

Since $\rho^{\lambda\sigma} = \rho_0^{\sigma}$ at the solution point, we must take the limit of $\lambda\to\infty$. We then identify Eqs. (72) and (73) as the UKS and UHFKS orbital equations, respectively, with asymptoti-

cally vanishing exchange-correlation and correlation potentials, $\lim_{\lambda\to\infty}\overline{v}_{\rm xc}^{\lambda\sigma}(\mathbf{r}_1)$ and $\lim_{\lambda\to\infty}\overline{v}_{c}^{\lambda\sigma}(\mathbf{r}_1)$. Of course in Eqs. (72) and (73) we do not expect the orbitals to be the same, though we have not used different suffices to avoid excessive notation. Note also, that in the general UHyKS orbital equation, the exchange operator would simply be multiplied by ζ.

For our closed shell input densities we use Brueckner doubles coupled cluster densities, and for open shell systems we used unrestricted MP2 input densities, using Gaussian TZ2P basis sets that are Dunning contractions[27] of Huzinaga primitive sets,[28] with additional polarization functions, as implemented in CADPAC.[29] All densities are ''relaxed'' in the sense that they correspond to the density matrix used when evaluating derivatives of the Brueckner doubles energy.

Because we only use a finite basis set to solve the orbital equations (72), (73), the correlated density is not exactly representable by a single Kohn–Sham determinant. Consequently, we must perform the calculation at some finite $\lambda_{\rm opt}$ to avoid diverging eigenvalues and potentials. Our previous investigations, suggest an optimum value of $\lambda_{\rm opt}=900$. We use this value here for all systems. Also, molecular calculations were performed at the experimental geometries.[30]

B. The computation of ensemble quantities

We now propose that given I^σ and A^σ, and $\overline{\epsilon}^\sigma_{\rm LUMO}$, $\overline{\epsilon}^\sigma_{\rm HOMO}$, $\overline{I}^\sigma_r$, and $\overline{A}^\sigma_r$, calculated using the numerical exchange-correlation and correlation potentials of the previous section, we can, using Eqs. (45), (46), (50), (60), calculate the asymptotic limits, $C^\sigma_{\rm xc}$, C^σ_c, and the hardness shifts, $\Delta^\sigma_{\rm xc}$ and Δ^σ_c through,

$$C^\sigma_{\rm xc}=-\tfrac{1}{2}[I^\sigma+A^\sigma+\epsilon^\sigma_{\rm LUMO}+\epsilon^\sigma_{\rm HOMO}], \tag{76}$$

$$C^\sigma_c=\tfrac{1}{2}[I^\sigma_r+A^\sigma_r-I^\sigma-A^\sigma], \tag{77}$$

$$\Delta^\sigma_{\rm xc}=\tfrac{1}{2}[I^\sigma-A^\sigma+\epsilon^\sigma_{\rm HOMO}-\epsilon^\sigma_{\rm LUMO}], \tag{78}$$

$$\Delta^\sigma_c=\tfrac{1}{2}[I^\sigma-A^\sigma+A^\sigma_r-I^\sigma_r]. \tag{79}$$

The range of systems accessible is limited to those for which we have data for I^σ and A^σ. Here we used experimental first ionization energies I and first electron affinities A for the ten systems—six closed shell, F_2, CO, HF, N_2, H_2, and HCl, and four open-shell, B, C, F, and O. For the closed shell systems, I and A are I^σ and A^σ, respectively. For the open shell systems B and C, I and A are I^α and A^α, respectively, and for O and F, I and A are I^β and A^β, respectively, where we have used the convention of Sec. II A, that is $N^\alpha\geqslant N^\beta$.

The calculations of $\epsilon^\sigma_{\rm HOMO}$ and $\epsilon^\sigma_{\rm LUMO}$ were performed by doing a self-consistent density functional calculation, without using an exchange-correlation functional, but by directly constructing the Fock matrix on a large grid using the numerical exchange-correlation potentials computed in Sec. III A. I^σ_r and A^σ_r were computed by performing a three point self-consistent Hartree–Fock calculation on the atoms, cations, and anions, again constructing the Fock matrix on a large grid with the additional numerical correlation potential of Sec. III A.

In addition, since Eqs. (45), (46), (50), and (60) are only strictly correct for vertical ionization energies and electron affinities, we have attempted to compute a crude correction to our input molecular experimental (nonvertical) ionization energies and electron affinities, giving $I^\sigma_{\rm corrected}$ and $A^\sigma_{\rm corrected}$. The UHF energy curve is approximately parallel to the true potential energy curve, in the region of the equilibrium geometry.[31] We thus calculate the UHF/TZ2P nonvertical ionization energies $I^\sigma_{\rm nv}$ and electron affinities $A^\sigma_{\rm nv}$ using the fully relaxed geometries for the cations, neutral molecules, and anions, and also the vertical UHF/TZ2P ionization energies I^σ_v and electron affinities A^σ_v (using the equilibrium molecular geometry), and take the difference between the vertical and nonvertical UHF ionization energies and electron affinities as a correction to the molecular ionization energies and electron affinities. Thus,

$$I^\sigma_{\rm corrected}=I^\sigma+I^\sigma_v-I^\sigma_{\rm nv}, \tag{80}$$

$$A^\sigma_{\rm corrected}=A^\sigma+A^\sigma_v-A^\sigma_{\rm nv}. \tag{81}$$

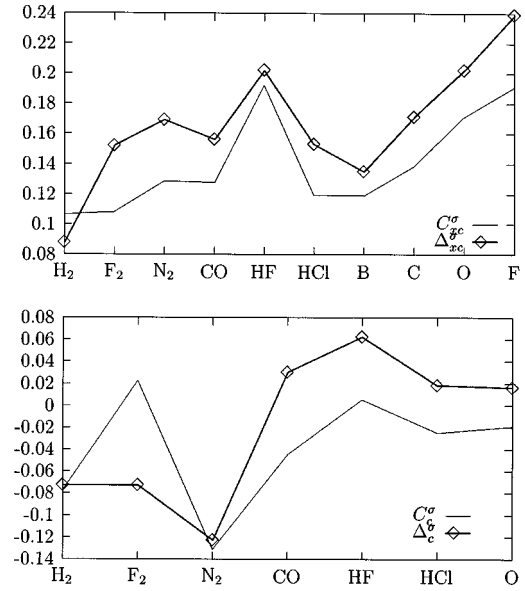

FIG. 2. (a) The quantities $C^\sigma_{\rm xc}$ (76) and $\Delta^\sigma_{\rm xc}$ (78) for several atomic and molecular systems, without the UHF correction, in atomic units, $E_{\rm h}$. Note that in the case of B and C, $\sigma=\alpha$, while for F and O, $\sigma=\beta$. (b) The quantities C^σ_c (77) and Δ^σ_c (79) for several atomic and molecular systems, without the UHF correction, in atomic units, $E_{\rm h}$. Note that in the case of O, $\sigma=\beta$.

C. Features of the asymptotic potentials and hardness shifts

In Figs. 2(a) and 2(b) we present plots of $C^\sigma_{\rm xc}$ and $\Delta^\sigma_{\rm xc}$, and C^σ_c and Δ^σ_c, respectively, with values tabulated in Table I, while in Figs. 3(a) and 3(b), we present the corresponding plots using the UHF correction for vertical ionization energies and electron affinities, with the values tabulated in Table II.

Note that for the atoms B and C, since we only had input I^α and A^α, calculated quantities refer to the case $\sigma=\alpha$ only, and similarly for O and F, the quantities are for the case $\sigma=\beta$. Also, the data for the correlation quantities for the atoms B, C, and F is not presented. This is because we had difficulty with the Zhao–Morrison–Parr procedure outlined

TABLE I. The UKS asymptotic potential C_{xc}^{σ} (76) and hardness shift $\Delta_{\mathrm{xc}}^{\sigma}$ (78), and the UHFKS asymptotic potential C_c^{σ} (77) and hardness shift Δ_c^{σ} (79), in atomic units, E_{h}. Note that for B and C, $\sigma=\alpha$, while for F and O, $\sigma=\beta$. See Secs. III B and III C for more details.

	C_{xc}^{σ}	$\Delta_{\mathrm{xc}}^{\sigma}$	C_c^{σ}	Δ_c^{σ}
H_2	0.107	0.088	−0.077	−0.073
F_2	0.108	0.152	0.023	−0.073
N_2	0.128	0.169	−0.131	−0.123
CO	0.127	0.156	−0.045	0.030
HF	0.192	0.202	0.005	0.062
HCl	0.119	0.153	−0.025	0.018
C	0.139	0.171		
F	0.191	0.239		
B	0.119	0.135		
O	0.170	0.202	−0.019	0.016

above, which did not give a potential corresponding to a ground state, but instead to some excited state with the same density as the input density.

As we might expect from Secs. II C and II D, $\Delta_{\mathrm{xc}}^{\sigma}$ and C_{xc}^{σ} are an order of magnitude greater than Δ_c^{σ} and C_c^{σ}. In some species, such as the atoms, where the HOMO-LUMO gap is small, $\Delta_{\mathrm{xc}}^{\sigma}$ is almost as large as the hardness itself. This again demonstrates that the hardness (and likewise the band gap) cannot come from a single Kohn–Sham calculation.

We see that $\Delta_{\mathrm{xc}}^{\sigma}$ and C_{xc}^{σ} are always positive; confirming earlier arguments put forth by Perdew *et al.*[11,12] drawing on work from von Barth,[32] that C_{xc} (the spinless counterpart) should be positive. Δ_c^{σ} and C_c^{σ}, on the other hand, oscillate between positive and negative values, and are very small.

A measure of the accuracy of our calculations is given by the agreement between $\Delta_{\mathrm{xc}}^{\sigma}$ and C_{xc}^{σ}, which from Eq. (53), should be equal. The graphs are qualitatively the same,

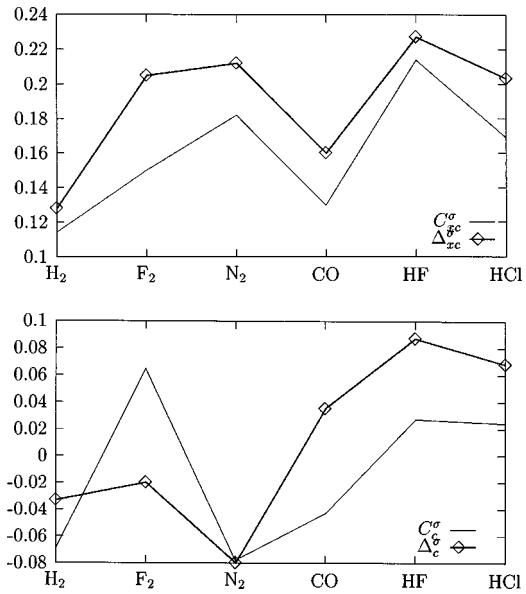

FIG. 3. (a) The quantities C_{xc}^{σ} (76) and $\Delta_{\mathrm{xc}}^{\sigma}$ (78), recalculated with the UHF correction (80), (81), in atomic units, E_{h}. Note that in the case of B and C, $\sigma=\alpha$, while for F and O, $\sigma=\beta$. (b) The quantities C_c^{σ} (77) and Δ_c^{σ} (79), recalculated with the UHF correction (80), (81), in atomic units, E_{h}. Note that in the case of O, $\sigma=\beta$.

TABLE II. The UKS asymptotic potential C_{xc}^{σ} (76) and hardness shift $\Delta_{\mathrm{xc}}^{\sigma}$ (78), and the UHFKS asymptotic potential C_c^{σ} (77) and hardness shift Δ_c^{σ} (79), using the UHF correction (80), (81) for molecules. Also tabulated is $C_{\mathrm{BLYP}}^{\sigma}$ (84) (using the UHF correction). Values of $\delta_{\mathrm{xc}}^{\sigma}$ for the atoms are included for reference. Note that for B and C, $\sigma=\alpha$, while for F and O, $\sigma=\beta$. See Secs. III B, III C, and IV for more details. Units are atomic units, E_{h}.

	$C_{\mathrm{xc}}\sigma$	$\Delta_{\mathrm{xc}}^{\sigma}$	C_c^{σ}	Δ_c^{σ}	$C_{\mathrm{BLYP}}^{\sigma}$
H_2	0.114	0.128	−0.069	−0.033	0.222
F_2	0.150	0.205	0.065	−0.020	0.245
N_2	0.182	0.212	−0.078	−0.080	0.190
CO	0.130	0.160	−0.043	0.035	0.190
HF	0.214	0.227	0.027	0.087	0.249
HCl	0.169	0.203	0.024	0.068	0.181
C		0.171			0.198
F		0.239			0.367
B		0.135			0.157
O		0.202			0.227

and the absolute agreement is fair, with a maximum deviation in the case of F_2 of a few tens of millihartrees. There is also qualitative agreement between Δ_c^{σ} and C_c^{σ}, which are related by Eq. (63). We believe that the large basis set and numerical grids used in this study, are sufficient for our calculations in the previous section of $\overline{\epsilon}_{\mathrm{HOMO}}^{\sigma}$, $\overline{\epsilon}_{\mathrm{LUMO}}^{\sigma}$, I_r^{σ}, and A_r^{σ}. Instead the the errors arise from the experimental data and ionization energies, which are only accurate (for the molecules) to a few tens of millihartrees, and are nonvertical. Another large source of error is the inaccuracy in the numerical potentials of Sec. IV A, which give ionization energies to within only a few tens of millihartrees. With this in mind, we should not be too concerned with the absolute accuracy of these results, in particular for C_c^{σ} and Δ_c^{σ}.

Using the UHF correction to the experimental I and A, we see that the agreement between $\Delta_{\mathrm{xc}}^{\sigma}$ and C_{xc}^{σ} is not really improved. Instead the effect of the correction is to uniformly increase $\Delta_{\mathrm{xc}}^{\sigma}$, C_{xc}^{σ}, Δ_c^{σ}, and C_c^{σ}. The magnitudes of the corrected C_{xc}^{σ} and C_c^{σ} are then similar to the values of the shifts in the numerical $v_{\mathrm{xc}}^{\sigma}(\mathbf{r})$ and $v_c^{\sigma}(\mathbf{r})$ used by Tozer and Handy,[33,34] and Chan, Tozer and Handy,[26] to fit the exchange-correlation and correlation functionals.

IV. IMPLICATIONS FOR EXISTING AND NEW FUNCTIONALS

In the previous sections, we have presented an account of the ensemble density functional theory. The implications of the nonzero value of $\Delta_{\mathrm{xc}}^{\sigma}$ and Δ_c^{σ} for hardness and band gap calculations has already been discussed. Here we will discuss the relevance of the nonvanishing asymptotic limits C_{xc}^{σ} and C_c^{σ}, to existing functionals, and for the construction of new ones. We will present our argument for the exchange-correlation functional, but the conclusions are equally applicable to the HyKS/HFKS correlation functional.

(1) *A statement frequently made in the literature is*

$$\lim_{r\to\infty} v_{\mathrm{xc}}^{\sigma}(\mathbf{r})=0. \tag{82}$$

Existing functionals are constructed to satisfy this condition. However, our calculations in the previous section

show that C^{σ}_{xc} is by no means negligible. How is Eq. (82) reconciled with the results of sec. II D, and in particular Eq. (47)?

First, there is flexibility in the definition of $v^{\sigma}_{\mathrm{xc}}(\mathbf{r})$. As mentioned earlier, $v^{\sigma}_{\mathrm{xc}}(\mathbf{r})$ is really only defined up to a constant, and its asymptotic limit is only precisely given under specific conditions. In particular, if we work within the grand canonical ensemble formalism, the definition of $\mu^{\sigma}(N^{\alpha\beta})$ in Eq. (11), though appealing, is by no means unique, and through choosing a different definition of the chemical potential μ^{σ}, we can define our exchange-correlation potential, for example, thus

$$v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r}) = v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})_{-}, \tag{83}$$

which satisfies Eq. (82). Alternatively, we could forsake an ensemble formulation altogether, and work within fixed $N^{\alpha\beta}$, in which

$$v^{\sigma}_{\mathrm{xc}} = \left(\frac{\delta E_{\mathrm{xc}}[\rho^{\alpha\beta}]}{\delta\rho^{\sigma}}\right)_{N^{\alpha\beta}}. \tag{84}$$

By virtue of the explicit constraint, $v^{\sigma}_{\mathrm{xc}}(\mathbf{r})$ in Eq. (84) will only be defined to within an arbitrary constant, which we can choose to satisfy Eq. (82). We note again that the constants that concern us, such as C^{σ}_{xc}, or the constant in Eq. (84), are independent of the ''trivial additive constant'' in the original Hohenberg–Kohn theorem.

However, given the ill-defined nature of $v^{\sigma}_{\mathrm{xc}}(\mathbf{r})$ at the integer, when constructing new functionals, which have well defined $v^{\sigma}_{\mathrm{xc}}(N^{\alpha\beta},\mathbf{r})$, what definition do we choose, and what conditions should we satisfy? Existing functionals are based on the local density approximation, and generally also involve some gradient expansion in the density (GGAs).[6] They are size consistent spatial integrals of functions of ρ^{σ} (and its gradients). Within an ensemble treatment, which we are justified in using, as the functionals are implicitly defined for noninteger fragment densities, we note that such GGAs are smooth functionals at $N^{\alpha\beta}$. We therefore expect to recover some $v^{\sigma}_{\mathrm{xc}}(\mathbf{r})$ which averages the left and right derivatives of the exchange-correlation functional, which is of course, precisely the definition which follows from Eq. (11). These approximate potentials will not vanish asymptotically, but should satisfy Eq. (47), at least as far as the energetically important regions of the systems extend. In particular, the key is to realize that although we can construct functionals, that when fed the exact density, give good energies, the need to capture good behavior off the integer is necessary if we wish to use our functional in a *variational* calculation. For example, we do not wish to minimize the energy of some atomic system by allowing the flow of charge into widely separated noninteger fragments!

(2) *How then do we explain the success of existing functionals? Must we satisfy the condition (82) if we use a finite grid?*

In practice, to facilitate integration, density functional calculations are carried out on some numerical grid. In such a discretized version of density functional theory, it is only important that the limits on the asymptotic potentials set out in Sec. II D are satisfied at the outermost grid points. In support of this, Tozer[35] has presented evidence that in the energetically important regions of hydrogenic systems, existing functionals yield potentials that are shifted upwards in rough accord with Eq. (47), and this may be why they give good energies. Indeed it has been known for some time[11] that $\epsilon^{\sigma}_{\mathrm{HOMO}}$ values calculated with existing functionals, are significantly shifted. In Fig. 4, we compare plots of $C^{\sigma}_{\mathrm{BLYP}}$, defined by

$$C^{\sigma}_{\mathrm{BLYP}} = \epsilon^{\sigma}_{\mathrm{HOMO}} + I^{\sigma}, \tag{85}$$

where $\epsilon^{\sigma}_{\mathrm{HOMO}}$ is from UKS calculations with BLYP,[36] with $\Delta^{\sigma}_{\mathrm{xc}}$ (using the UHF correction for nonvertical input ionization energies and electron affinities). The values are tabulated in Table II. The agreement between the shifts in the HOMO eigenvalues, with the hardness shift $\Delta^{\sigma}_{\mathrm{xc}}$ we have calculated is very suggestive. Existing functionals seem to already incorporate the constraint (47) in a limited fashion.

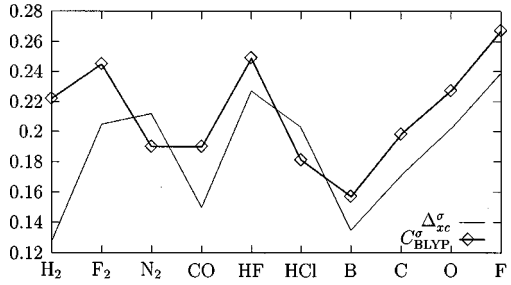

FIG. 4. The shift in the BLYP HOMO eigenvalue $C^{\sigma}_{\mathrm{BLYP}}$ (85) plotted against $\Delta^{\sigma}_{\mathrm{xc}}$ (78), both with the UHF correction (80), (81), in atomic units, E_{h}. Note that in the case of B and C, $\sigma=\alpha$, while for F and O, $\sigma=\beta$.

Perhaps the most striking example of the need to satisfy Eq. (47) comes from the work of Handy *et al.*[26,33,34] They demonstrated that functionals constructed to fit the numerical exchange-correlation potentials and correlation potentials of Sec. III A, that satisfied Eq. (82), gave extremely poor energies; however if they fitted to accurate potentials that satisfied Eq. (47), they could obtain energies comparable to the best existing functionals.

(3) *The grand canonical ensemble theory described here, is not the only way to treat noninteger particle numbers. In fact, the derivative discontinuities arise only from the ensemble treatment.*

Since there are no real physical closed *system* densities with noninteger particle numbers, the energy of such systems is not really well defined, and thus there are arbitrarily many ways to define the map between noninteger densities and the corresponding energies, some of which can be maps without discontinuities. This has been exploited by many authors, including Landau,[37] Slater,[38] Janak,[16] and most recently Nesbet.[39] However, the ZTGC treatment of noninteger systems (as in this work) is important, as the requirement that the total energy of well-separated fragments always sums to the total energy of the complete system, for any fragment densities, is only fulfilled if the energy of the fragments is treated using the ensemble theory of open systems.[10,11]

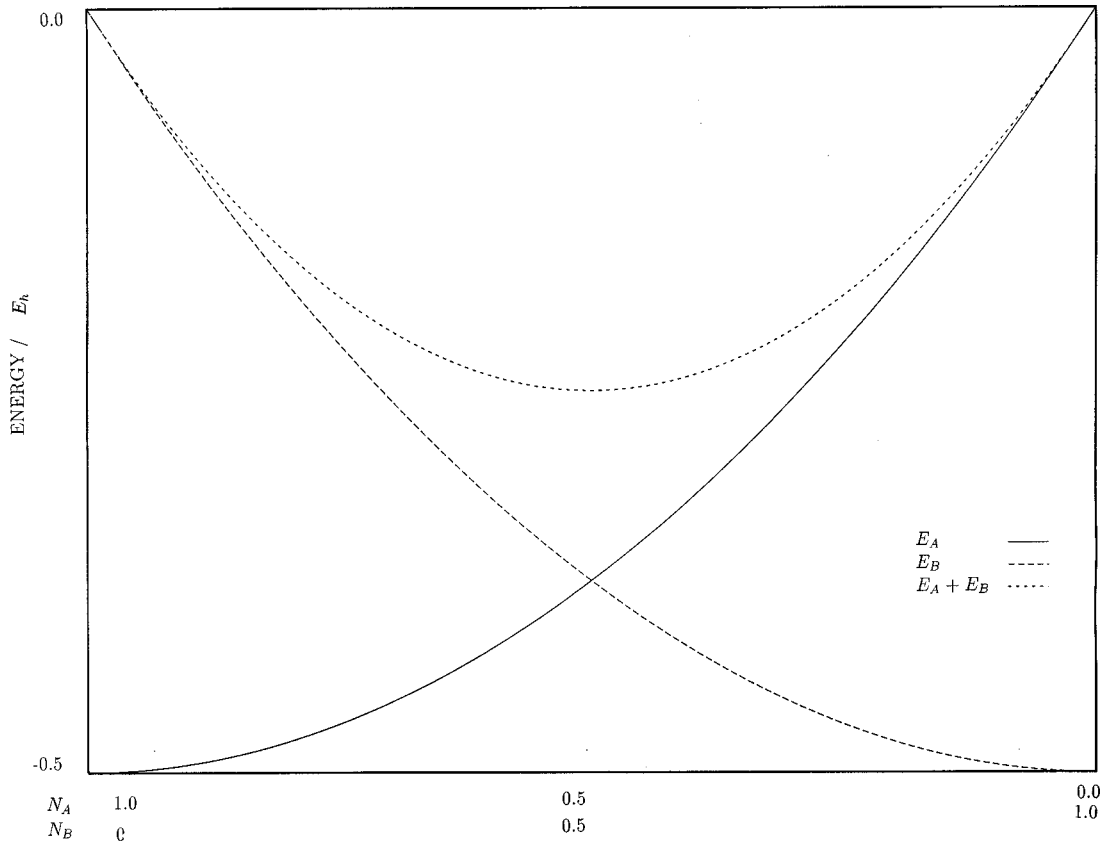

FIG. 5. A schematic diagram of the energy of a one-electron system of hydrogens H_A and H_B, with energies E_A and E_B and particle number N_A and N_B, in the limit of infinite separation, calculated with some smooth functional. See Sec. IV.

Recall in Sec. II A, we hinted at this requirement. Thus we can choose the size-consistent map between noninteger densities and their properties, such as total energies, to be defined by the map between noninteger fragment densities and their properties, as we have done here.

In practice, the GGA functionals we work with, being size-consistent integrals, impose a restriction on the noninteger (density-total energy) maps, that they also be size consistent. This does not imply that the GGA functionals are necessarily good approximations to the exact ensemble energy functional; a continuum approximation will not exhibit derivative discontinuities, nor do GGAs satisfy the sum-rule for the exchange-correlation hole for noninteger particle numbers.[12] However, it does mean that we can judge a GGA by the accuracy with which it ''mimics'' the behavior of the exact ensemble energy functional [for example, as discussed in point (2) above] both on *and* off the integer, and thus the analysis presented here is relevant to their improvement.

Finally, we note that if we restrict ourselves to only integer densities, and number-conserving variations, the density-total energy maps still contain derivative discontinuities, e.g., if we sum two density fluctuations of order *dn* in particle number, on widely separated atoms, such that the total ground-state fluctuation is number *conserving*, the change in energy can still be of order $|dn|$.[10] The derivative discontinuities are not an artifact of the restrictive nature of the ZTGC, but are a manifestation of Fermi-statistics.[40] Using an ensemble formulation, as we have done here, only makes the discontinuities more transparent.

We conclude that it is most important to take into account the results of the ensemble theory, and particularly C_{xc}^{σ}, when constructing new functionals. In practice, we need not necessarily explicitly take into account the nonsmoothness of the exchange-correlation functional. It certainly may be possible to construct a (nonunique) smooth exchange-correlation functional, that yields ground-state $N^{\alpha\beta}$ densities and energies for *extremal* (rather than minimal) solutions of the Euler–Lagrange equation (3). The functionals constructed by Handy *et al.*,[26,34] constructed by fitting to potentials, are most likely approximations to such a smooth functional. A smooth formulation would also be important for the functional expansions of Liu and Parr,[41] which assume the existence of all functional derivatives at $N^{\alpha\beta}$.

There will, however, be cases where a smooth functional can be expected to fail spectacularly. One such case is the dissociation of the one electron molecule ion, H_2^+. We are not the first to consider this system, and the failure of existing (smooth) functionals to give the correct ground state at infinite separation (which instead predict a minimum for the system with half an electron on either hydrogen), has previously been interpreted in terms of noncomplete cancellation of the self-repulsion term. Greater insight can be gained,

however, by considering the infinitely separated hydrogens, H_A and H_B as open systems, with energies E_A and E_B, and particle numbers N_A and N_B, respectively. Plotted in Fig. 5 is a schematic curve of the energy of the two open systems as density is transferred from one hydrogen to the other, for some smooth exchange-correlation functional (such as LDA). We see that any size-consistent convex (in N) functional which does not predict a linear interpolation between $E(N)$, will always minimize with half a positive charge on each hydrogen, at a lower energy than that of the infinitely separated atom and ion. In such a case we are forced to use a more sophisticated, nonsmooth functional, such as an orbital functional, of which Hartree–Fock exchange is an important example.

V. CONCLUSIONS

Although the initial work in this area of ensemble theory is more than a decade old, the results are not as widely known as they should be, especially in the molecular physics community. In particular, the influence of exact exchange, was previously unknown.

Part of this stems from the lack of hard numerical data concerning the asymptotic exchange correlation and correlation potentials C_{xc}^{σ} and C_c^{σ} and the hardness shifts $\Delta_{\mathrm{xc}}^{\sigma}$ and Δ_c^{σ}, in atomic and molecular systems. Certainly the effects are more subtle and less obvious in finite systems than in infinite systems.

Here we have taken a fresh look at the ensemble density functional theory, and shown how it can easily be extended to a practical spin-density formulation. The theory of the various manifestations in unrestricted Kohn–Sham and unrestricted hybrid Kohn–Sham theory, such as the hardness shifts $\Delta_{\mathrm{xc}}^{\sigma}$, Δ_c^{σ}, and the nonvanishing asymptotic potentials C_{xc}^{σ}, C_c^{σ} have been presented in a form ready for computation. We have presented and implemented a general method, using experimental ionization energies and electron affinities, and reference system data calculated from numerical potentials obtained from *ab initio* data, to calculate $\Delta_{\mathrm{xc}}^{\sigma}$, Δ_c^{σ}, C_{xc}^{σ}, and C_c^{σ}. Although these quantities are small, they are by no means negligible.

We have also discussed the importance of incorporating C_{xc}^{σ} and C_c^{σ} information into new exchange-correlation and correlation functionals, and clarified what it means to have an asymptotic nonvanishing potential in an approximate functional. We have also suggested that nonvanishing asymptotic potentials, are already incorporated into existing functionals in a limited way. We believe that a full consideration of the results of the ensemble theory will become increasingly important for the construction of future functionals.

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APPENDIX A

Here we discuss some properties of $\delta E/\delta\rho^{\sigma}$. Recall the definition of the functional derivative

$$dE = \int \frac{\delta E[\rho]}{\delta\rho^{\sigma}(\mathbf{r})}\,\delta\rho^{\sigma}(\mathbf{r})\,d\mathbf{r}, \tag{A1}$$

where $\delta\rho^{\sigma}(\mathbf{r}) = \epsilon f(\mathbf{r})$, and the derivative is defined in the limit $\epsilon \to 0_+$. $f(\mathbf{r})$ may be considered as the determining the path along which we define the derivative, and choosing different $f(\mathbf{r})$ is an extension of the concept of choosing left and right limits in the usual derivatives of functions.

For well behaved functionals, $\delta E/\delta\rho^{\sigma}$ is independent of $f(\mathbf{r})$. However, if E is not smooth at $\rho_0^{\alpha\beta}(\mathbf{r})$, say, then the functional derivative $[\delta E/\delta\rho^{\sigma}]_{\rho_0^{\alpha\beta}}$ becomes *path-dependent*; that is, it depends on the choice of $f(\mathbf{r})$.

In this work, when we write an equality such as in Sec. II A,

$$\frac{\partial E_0}{\partial M^{\sigma}} = \left(\frac{\delta E}{\delta\rho^{\sigma}}\right)_{\rho_0^{\alpha\beta}}, \tag{A2}$$

where we are considering derivatives of the *ground-ensemble energy*, we are defining the functional derivative $[\delta E/\delta\rho^{\sigma}]_{\rho_0^{\alpha\beta}}$ *along the path of ground-ensemble densities*. This is the path we choose to work with here.

Similarly, left and right functional derivatives, as in Sec. II C, are defined as the left and right derivatives along the path of ground state densities.

APPENDIX B

Here we outline the extension of Janak's theorem to exact exchange systems. We follow the original derivation,[16] to which the reader is referred for detailed discussion.

Partition the energy in terms of extended orbital functionals,

$$E[\rho^{\alpha\beta}] = \min_{n_i^{\sigma},\phi_i^{\sigma}} \langle \hat{T}_j + \hat{J}_j + \zeta\hat{K}_j\rangle + E_{cj}[\rho^{\alpha\beta}] + \int \rho(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}), \tag{B1}$$

where the minimization over $[n_i^{\sigma},\phi_i^{\sigma}]$ is constrained to reproduce the ground state σ spin density $\rho_0^{\sigma}(\mathbf{r})$, given by

$$\rho_0^{\sigma}(\mathbf{r}) = \sum_i^m n_i^{\sigma}[\phi_i^{\sigma}(\mathbf{r})]^2. \tag{B2}$$

The number of orbitals m is arbitrary, but must be not less than N^{σ}. To make contact with ensemble theory later, we will consider the case where the number of orbitals is the integer closest to, but not less than N^{σ}. Moreover, the distribution numbers are chosen as are $n_{i\neq \mathrm{HOMO}}^{\sigma} = 1$, $n_{\mathrm{HOMO}}^{\sigma} \leqslant 1$.

T_j, J_j, and K_j are defined in the spirit of the original Janak generalization,

$$T_j[\rho^{\alpha\beta}] = \sum_{i\sigma} n_i^{\sigma}\langle\phi_i^{\sigma}| -\tfrac{1}{2}\nabla^2|\phi_i^{\sigma}\rangle, \tag{B3}$$

$$J_j[\rho^{\alpha\beta}]=\int\int \frac{1}{2}\sum_{ij\sigma\sigma'} n_i^{\sigma} n_j^{\sigma'}[\phi_i^{\sigma}(\mathbf{r}_1)]^2 \times\frac{1}{r_{12}}[\phi_j^{\sigma'}(\mathbf{r}_2)]^2 d\mathbf{r}_1 d\mathbf{r}_2, \tag{B4}$$

$$K_j[\rho^{\alpha\beta}]=-\int\int \frac{1}{2}\sum_{ij\sigma} n_i^{\sigma} n_j^{\sigma}\phi_i^{\sigma}(\mathbf{r}_1)\phi_j^{\sigma}(\mathbf{r}_2) \times\frac{1}{r_{12}}\phi_i^{\sigma}(\mathbf{r}_2)\phi_j^{\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \tag{B5}$$

Note that since $E[\rho^{\alpha\beta}]$ is the true energy of the system, the Janak ζ dependent correlation energy functional $E_{cj}[\rho^{\alpha\beta}]$ is defined by Eq. (B1). Additionally, since the density is given by a sum of a single set of orbitals, unlike the UHyKS orbital decomposition of Eq. (30), $T_j[\rho^{\alpha\beta}]$, $J_j[\rho^{\alpha\beta}]$, and $K_j[\rho^{\alpha\beta}]$, defined by the Janak generalization, will be numerically different from the UHyKS functionals, $T_r[\rho^{\alpha\beta}]$, $J_r[\rho^{\alpha\beta}]$, and $K_r[\rho^{\alpha\beta}]$, except at $N^{\alpha\beta}$. Consequently $E_{cj}[\rho^{\alpha\beta}]$ is different to $E_c[\rho^{\alpha\beta}]$.

Then for a given set of n_i^{σ}, we can carry out the minimization in Eq. (B1) explicitly with respect to the spin orbitals, preserving orthonormality with the usual diagonal constraints, giving

$$\frac{\delta}{\delta\phi_i^{\sigma *}}\left[E[\rho^{\alpha\beta}]-\sum_{i\sigma}(\epsilon_i^{\sigma}\langle\phi_i^{\sigma}|\phi_i^{\sigma}\rangle-1)\right]=0. \tag{B6}$$

Since, by our choice above, $n_i^{\sigma}\neq 0$, the above yields, after dividing through by n_i^{σ}, the orbital equation,

$$\left[-\frac{1}{2}\nabla^2+\sum_{j\sigma'} n_j^{\sigma'}\int\frac{[\phi_j^{\sigma'}(\mathbf{r}_2)]^2}{r_{12}}d\mathbf{r}_2-\zeta\sum_j n_j^{\sigma} \times\int\frac{\phi_j^{\sigma}(\mathbf{r}_1)\phi_j^{\sigma}(\mathbf{r}_2)}{r_{12}}P_{12}d\mathbf{r}_2+v_c^{\sigma}(\mathbf{r}_1)+v_{\mathrm{ext}}(\mathbf{r}_1)\right]\phi_i^{\sigma} =\epsilon_i^{\sigma}\phi_i^{\sigma}, \tag{B7}$$

where $v_{cj}^{\sigma}(\mathbf{r})$ is simply $\delta E_{cj}/\delta\rho^{\sigma}$. For integer occupation numbers, Eq. (B7) reduces to the UHyKS orbital equation, with the exception of a possible constant in the potential.

Next, to obtain Janak's theorem, we must relate the orbital eigenvalue to the derivative of the energy. Differentiating the energy expression (B1), using Eqs. (B3), (B4), (B5), with respect to n_i^{σ},

$$\frac{\partial E}{\partial n_i^{\sigma}}=\langle\phi_i^{\sigma}|-\frac{1}{2}\nabla^2+\sum_{j\sigma'} n_j^{\sigma'}\int\frac{[\phi_j^{\sigma'}(\mathbf{r}_2)]^2}{r_{12}}d\mathbf{r}_2 -\zeta\sum_j n_j^{\sigma}\int\frac{\phi_j^{\sigma}(\mathbf{r}_1)\phi_j^{\sigma}(\mathbf{r}_2)}{r_{12}}P_{12}d\mathbf{r}_2+v_{cj}^{\sigma}(\mathbf{r}_1) +v_{\mathrm{ext}}(\mathbf{r}_1)|\phi_i^{\sigma}\rangle \tag{B8}$$

$$=\epsilon_i^{\sigma}. \tag{B9}$$

This is the corresponding Janak's theorem for exact exchange systems.

At this point, it is possible, with the choice of occupation numbers above, to make the following identity

$$\frac{\partial E}{\partial n_{\mathrm{HOMO}}^{\sigma}}=\frac{\partial E}{\partial N^{\sigma}}. \tag{B10}$$

Note that, where the energy is differentiable, we now have

$$\epsilon_{\mathrm{HOMO}}^{\sigma}(N^{\alpha\beta}+\omega^{\sigma})=-A^{\sigma}(N^{\alpha\beta}), \tag{B11}$$

$$\epsilon_{\mathrm{HOMO}}^{\sigma}(N^{\alpha\beta}-\omega^{\sigma})=-I^{\sigma}(N^{\alpha\beta}). \tag{B12}$$

It is not surprising that these results differ from the UHyKS results, since off the integer, the quantities T_j, J_j, K_j, and E_{cj} differ from T_r, J_r, K_r, and E_c.

We feel that the generalization of the UHyKS correlation functional through the ensemble theory of Sec. II B is somewhat more intuitive than using the Janak generalization, although the two agree, by construction at $N^{\alpha\beta}$.

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